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Temperature Dependence of Electron Transfer in the Unsolvated Trinuclear Iron Carboxylate, $[\text{Fe}_3\text{O}(\text{piv})_6(\text{C}_4\text{N}_2\text{H}_5)_3]$.

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Beamline(s): X3A1

Introduction: Our continued studies of the temperature dependence of the electron transfer (ET) in the class of mixed-valence trinuclear carboxylates [1] has led to the discovery of a number of new complexes [2]. So far, change of ET has been correlated with change of solvent or ligand structural disorder, in one case reported to be accompanied by a phase transition, which was caused by change in dynamics of a solvent benzene molecule [3]. The space group changed simultaneously. The title compound also exhibits a phase transition connected with the temperature dependent change of ET but without change of space group; instead the number of independent molecules in the structure doubles from one to two.

Methods and Materials: Single crystal X-ray diffraction data ($\lambda=0.643 \text{ \AA}$) of the title compound were collected with a Bruker SMART6000 CCD detector at beamline X3A1 at a crystal temperature of 16(5) K reached using a liquid He-cooling device. The complex crystallizes in the acentric space group $P2_1$ with $a = 13.593 \text{ \AA}$, $b = 19.777(1) \text{ \AA}$, $c = 19.463(1) \text{ \AA}$, $\beta = 90.909(1)^\circ$. A total of 199140 intensities ($(\sin(\theta)/\lambda)_{\text{max}} = 1.01 \text{ \AA}^{-1}$) were collected, which were reduced to 65190 unique reflections, $R_{\text{int}}=0.027$.

Results: The two molecules (labelled A and B) in the low temperature form of the title complex are shown below. Above the phase transition temperature, there is severe dynamic disorder in the pivalate ligands and the ET involves all three iron atoms [2]. In contrast, in the studied low-temperature phase, one molecule (A) is completely valence trapped, while a small amount of ET still takes place in the other molecule (B) at 16 K, but now only between two of the three iron atoms. The most significant difference between molecules A and B is the rotation of the imidazole ligand (62.2°) coordinated to Fe(2) in A. We are currently modelling the electron density distribution in A and B from the synchrotron data.

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References:

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